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Non-Destructive Characterization of Polymer Interphases and In-Situ Polymerization Using Surface-Enhanced Raman Scattering

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The molecular structure of interphases between substrates such as metals and graphite and polymer systems cured against them was determined using surface analysis techniques such as reflection-absorption infrared spectroscopy, X-ray photoelectron spectroscopy, and surface enhanced Raman scattering. It was found that the substrates had a significant effect on the molecular structure of the interphase and that the molecular structure of the interphase was significantly different from that of the bulk polymers. In some cases, there was a vigorous reaction between components of the polymer system and the substrate. Thus, when an acrylic adhesive was cured against silver substrates, o-benzoic sulfimide, a component of the curing system, segregated to the interface and reacted with metal ions to form salts. The salts reacted with a peroxide in the curing system to form radicals which initiated polymerization. In other cases, components

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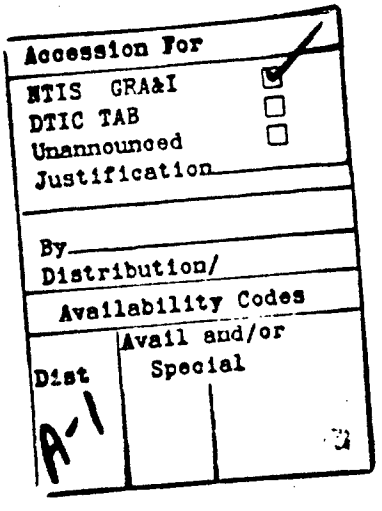
19. Abstract (continued)

of the polymer preferentially adsorbed onto the substrate. Thus the curing agent dicyandiamide was adsorbed at the interface between an epoxy and silver. The behavior of polyamic acids was strongly affected by substrates they were deposited on. When polyamic acids were deposited onto relatively inert substrates such as gold or highly oriented pyrolytic graphite, there was little interaction between the polymer and the substrate and thermal curing of the polyamic acid to the polyimide occurred readily. However, when polyamic acids were deposited onto silver, carboxylate ions formed and inhibited curing in the interphase. The poorly cured polymer in the interphase had a strong effect on the properties of adhesive bonds between polyimides and silver substrates. When polyimide films were delaminated from silver substrates, failure always occurred in the interphase, between the thin region of partially cured material at the silver surface and the well cured bulk of the films. It was thus concluded that substrates strongly effect the structure and properties of polymer systems cured against them.



I. Introduction

The goal of this research was to determine the molecular structure of interphases formed by polymer systems cured against metal substrates. We were particularly interested in obtaining fundamental information regarding catalysis or inhibition of polymerization reactions by metals, configurations of polymers adsorbed onto metals, preferential adsorption of components of polymer systems onto metals, mechanisms by which polymers and small molecules adsorb onto metals, extent of cure as a function of distance away from a metal surface and into a polymer cured against the metal, and migration of metal ions into polymers cured against the metals. Our approach was to use a variety of analytical techniques, including reflection-absorption infrared spectroscopy (RAIR) and x-ray photoelectron spectroscopy (XPS), to examine interphases between polymer systems and metal substrates.

However, we were especially interested in the use of surface-enhanced Raman scattering (SERS). SERS is a process in which the inelastic (Raman) scattering of visible light by molecules adjacent to the roughened surfaces of certain metals is enhanced as much as 10^6. The enhancement is great for molecules near the surface but decreases rapidly as a function of distance and vanishes for molecules only a few molecular layers away from the surface. As a result, the Raman signal from a thin polymer film on a SERS-active metal substrate arises mostly from the interface, not the bulk of the film, and SERS may be used for in-situ, non-destructive characterization of polymer/metal interphases.

II. Summary of Results

We examined the interphase between an acrylic adhesive and silver substrates and showed that the composition of the interphase was significantly different from that of the bulk adhesive (1,2). In particular, o-benzoic sulfimide, a component of the cure system, segregated to the interface where it reacted with metal ions to form salts. The metal ions in these salts could be alternately reduced or oxidized by acetylphenylhydrazine or cumene hydroperoxide, other components of the cure system. The step in which the metal ions were oxidized resulted in the formation of radicals which initiated polymerization of the monomer, triethylene glycol dimethacrylate.

We examined interphases between silver substrates and epoxy adhesive systems cured with dicyandiamide (3,4) and benzophenone tetracarboxylic dianhydride (5) and observed segregation of the curing agent to the interphase in both cases, again indicating that the molecular structure of the interphase was much different from that of the bulk adhesive system. It was observed that the curing agent BTDA adsorbed dissociatively at the silver surface to form carboxylate salts. Adsorption of the dicyandiamide curing agent involved coordination of the nitrilo nitrogen atom to the silver substrate.

One of our principal areas of investigation has concerned interphases between polyimides and silver, gold, and graphite substrates. We began this investigation by examining the adsorption of model compounds such as pyromellitic diimide (PMDI) and N, N - diphenyl pyromellitic diimide (DPPMDI) onto silver (6). We determined that PMDI was adsorbed dissociatively by the loss of one imide hydrogen atom and had a vertical conformation on the silver substrate. DPPMDI molecules were physisorbed onto silver and had a random orientation.

The results obtained for PMDI adsorbed onto highly oriented pyrolytic graphite (HOPG) substrates were much different. It was found that PMDI was adsorbed onto HOPG with a horizontal configuration in which the rings of the molecules were parallel to the surface (8). However, DPPMDI was randomly oriented on the HOPG surface (8).

Next we began an investigation of interphases between silver substrates and polyimides from pyromellitic dianhydride (PMDA) and oxydianline (ODA) and from PMDA and 2,2-bis(4-(4-aminophenoxy)-phenyl)-hexafluoropropane (BTDA) (8,9). When thin films of the polyamic acids of PMDA/ODA and PMDA/4-BDAF were spin-coated onto silver substrates, it was observed that the SERS spectra were independent of film thickness, demonstrating that the spectra were characteristic of the interface rather than the bulk of the films and that SERS was indeed *surface-selective*. Bands characteristic of carboxylate species were observed, indicating that the acid groups in the polyamic acids interacted with the substrates. When attempts were made to imidize the films on silver substrates, it was observed that the bands characteristic of amide groups and carboxylate species did not decrease in intensity and that only weak bands related to imide groups appeared in the SERS spectra, indicating that imidization was inhibited by formation of carboxylate species in the interphase.

Substantially different results were obtained using gold substrates. Little evidence for formation of carboxylate species between the polyamic acids and gold substrates was observed. Moreover, polyamic acids on gold substrates were easily cured to form the corresponding polyimides (10).

It was observed that failure of adhesive bonds between polyimides and silver substrates was very close to the interface but was always cohesive within the polyimide. This behavior was related to the poor state of cure of the polyimide adjacent to the silver substrate (11).

When XPS was used to examine interphases between the polyamic acid of PMDA/4-BDAF and highly oriented pyrolytic graphite (HOPG) substrates, the results obtained were similar to those for gold substrates. Little evidence for a chemical interaction was observed and curing of the polyamic acid to the polyimide was easily obtained (11).

During the course of this work, we found that certain chemical reactions could occur at the interface between silver and organic compounds during intense laser irradiation. One such reaction involved the oxidation of amines to nitro compounds and the reduction of the nitro compounds to form azo compounds (12).

Another reaction involved the oxidation of polymeric compounds to form graphite-like species (1). It was determined that these reactions could be suppressed by decreasing the intensity of laser irradiation and/or by carrying out SERS experiments in an inert environment.

III. Conclusions

The results obtained here are consistent with the following conclusions:

*Surface-enhanced Raman scattering (SERS) is a powerful technique for the *in-situ, non-destructive* characterization of interphases between polymers and SERS-active substrates such as silver, copper, and gold.

*The molecular structure of interphases between polymers and metals is significantly different from that of the bulk polymers.

*Low molecular weight compounds such as curing agents frequently segregate to the interface between a polymer system and a metal. Those compounds may react with metal ions in the substrate to form complexes as in the case of o-benzoic sulfimide contained in a model acrylic adhesive or benzophenone tetracarboxylic dianhydride contained in a model epoxy adhesive. In other cases, they may just adsorb onto the substrate, as in the case of dicyandiamide.

*Polyamic acids interact with metal ions on reactive metal substrates such as silver to carboxylate salts which inhibit curing of the polyamic acid to the polyimide in the interfacial region.

*Polyamic acids do not interact with metal ions on inert metal substrates such as gold. In such cases, curing of the polyamic acid to the polyimide in the interfacial region occurs readily. Similar behavior is observed on graphite substrates.

*Failure of adhesive bonds between polyimides and silver substrates is near the interface but is cohesive within the polyimide. This behavior is related to the poor state of cure of the polyimide adjacent to the metal substrate.

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